Sulfur Speciation of Desulfurized Coals by XANES Spectroscopy

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ABSTRACT

Least square analysis of the x-ray absorption near edge structure (XANES) region of sulfur K-edge x-ray absorption fine structure (XAFS) spectra can provide a quantitative analysis of both the organic and inorganic functional forms of sulfur in coal. In the current article, this method is applied to speciation of the sulfur forms in a number of desulfurized coals. The samples invesitgated include specimens treated with boiling perchlorethylene, samples subjected to selective chemical reactions, samples subjected to molten caustic leaching, and biologically desulfurized coals. In all cases, analysis of the XANES provides a reasonably quantitiative speciation of the changes in the sulfur forms resulting from the various treatments.

INTRODUCTION

In the past several years, it has been demonstrated that sulfur K-edge x-ray absorption fine structure (XAFS) spectroscopy can be used to speciate all of the major functional forms of sulfur. Two primary methods of analysis have been used: direct least squares analysis of the x-ray absorption near edge structure (XANES) [1-3] and a third derivative treatment of the XANES [4-6]. With the least squares analysis approach, it is possible to quantitatively determine the percentages of the total sulfur present in five principal organic functional forms and several inorganic forms with an accuracy of ±5-10%.

An obvious application of this capability is the investigation of the changes in sulfur forms produced by desulfurization treatments. Particularly of interest are treatments aimed at removing organic sulfur. In the current paper, we present the results of XANES analysis of coals subjected to a variety of chemical and biological desulfurization treatments.

EXPERIMENTAL PROCEDURE AND SAMPLE DESCRIPTION

The samples investigated were prepared in several laboratories. The desulfurization procedures have been described in detail elsewhere and will not be discussed here. Samples studied included coals treated by boiling perchlorethylene (PCE) prepared in the laboratories of Prof. Sunyu Lee[7] and Dr. Melissa Chou[8], specimens treated with single electron transfer and strongly basic reagents in the laboratory of Dr. Kuntal Chatterjee and Prof. Leon Stock [7-11], samples subjected to biological desulfurization by Dr. John Kilbane [12], and samples treated by molten caustic leaching [13] provided by Mr. Phil Goldberg of the Pittsburgh Energy Technology Center.

The sulfur K-edge XAFS spectroscopy was carried out at beamline X-19A at the

National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. To minimize x-ray absorption, the x-ray beam at X-19A is maintained in machine vacuum all the way from the synchrotron ring to the experimental hutch, and is thereafter is maintained in a helium atmosphere. All spectra were taken in the fluorescent mode using a Stearn-Heald ionization detector [14]. The x-ray energy was varied from approximately 100 eV below to about 400 eV above the sulfur K-shell absorption edge (2472 eV) using a Si (111) double crystal monochromator.

RESULTS AND DISCUSSION

Biologically Desulfurized Samples: Previously, we have used XANES to examine a number of biologically solubilized and desulfurized samples [2]. The primary conclusion of that earlier work was that biological agents did not discriminate greatly between different functional forms of sulfur, and little if any organic sulfur was removed by biological treatment. More recently, however, XANES has been used to examine several samples subjected to biotreatment using the microbe *Rhodococcus rhodochrous*, as discussed in detail elsewhere by Kilbane [12].

Typical fitted XANES spectra of a control sample and a biotreated sample of an Illinois #6 coal are shown in Figure 1. Prior to treatment, most of the pyrite was removed from the coal. The results are summarized in Table I and Figure 2. In both examples, it is seen that a substantial reduction in organic sulfur was accomplished. However, it is evident from Figure 2 that the relative amounts of the different functional forms of organic sulfur were essentially unchanged, within the standard error (±5%). It therefore appears that all of the organic sulfur functional forms were reduced approximately equally by the treatment [12].

Coals Subjected to Molten Caustic Leaching: A molten caustic leaching process for removal of both ash and sulfur from coal has been developed by TRW Corporation [13]. The fitted XANES obtained from a Kentucky #9 coal subjected to this process is shown in Figure 3. It is evident that the sulfur has undergone considerable oxidation. The results obtained by quantitative analyses of the XANES are summarized for three coals in Table 2: a Kentucky #9 coal and a Pittsburgh #8 coal subjected to the molten caustic leaching process, and the Pittsburgh #8 coal prior to leaching [1]. It is evident that the forms of sulfur are drastically changed and reduced by this rather severe process. In particular, no pyrite or organic sulfide remain, and thiophenic sulfur, which is the dominant organic sulfur form in the original coals is reduced to only about 0.1% in the treated coals. Elemental sulfur, sulfone, and sulfate are the dominant sulfur species remaining, indicating severe oxidation.

Perchlorethylene Treated Samples: We have examined a number of samples before and after treatment with PCE. For the samples investigated to date, it is concluded that the primary effect of the treatment is to remove elemental sulfur. Typical results for a number of samples are summarized in Table 3. It is seen that elemental sulfur is the primary sulfur form removed for all of the samples which exhibited a decrease in sulfur due to PCE treatment. It is also noted that all of these samples contain a significant amount of sulfate, indicative of substantial oxidation. In two cases, a fresh coal is compared to the sample before PCE treatment. It appears that an oxidative step is essential to produce the elemental sulfur that is removed by the PCE treatment. It is known that oxidation of pyrite will

produce both sulfate and elemental sulfur [15]. The current XANES data, however, have not included enough fresh coals before the oxidative step to conclude whether or not any significant amount of organic sulfur is being converted to elemental sulfur in this step. A more detailed paper is in preparation summarizing our results on PCE treated coals [16].

Coals Treated with Single Electron Transfer(SET) and Basic Reagents:

Chatterjee and Stock have discussed the removal of organic sulfur from coal by treatment with SET [9] and strongly basic reagents [10]. A suite of these desulfurized coals were previously examined by XANES spectroscopy by Chatterjee et al. using the third derivative method of XANES analysis developed by Gorbaty et al. [11]. We have examined the same suite of samples independently using the least squares analysis approach for deconvolution of the XANES. The results are summarized in Table 4.

The results for the raw Illinois no. 6 coal, obtained from the Argonne Premium Coal Sample Bank, are similar to those we have reported earlier [1], except for the presence of some sulfate. After treatment with lithium aluminum hydride (LAH), all of the pyrite and most of the sulfate have disappeared; additionally, the percentage of organic sulfide appears to have decreased relative to thiophenic sulfur. Following the SET treatment, the thiophenic sulfur percentage is significantly decreased, while the BASE treatment produces a substantial decrease in the sulfidic sulfur. This is exactly as proposed by Stock and Chatterjee [6,7] and as previously observed by the third derivative treatment of the XANES data of Gorbaty [11]. However, the results are obscured somewhat by the appearance of an unidentified sulfide which gives an s→p peak in the spectrum at -0.5 eV. Presumably, this is a potassium sulfide, in view of the nature of the chemical treatment. Since we have not conclusively identified this phase and have not determined a coefficient for conversion of its peak area percentage to sulfur percentage, we have simply assumed a conversion coefficient of 1.0 to derive the values in Table 4. This should not significantly affect the relative percentages of the other functional forms of sulfur, however.

For the samples treated with SET then BASE, and with BASE then SET, the thiophenic sulfur is markedly decreased in both cases, but there does not appear to be any decrease in the organic sulfide. In this regard, however, it should be noted that the accuracy of our method with an unknown inorganic sulfide present is not better than about ±10%.

The final two treatments indicated in Table 4 both produce significant sulfur oxidation and a decrease in thiophenic sulfur, by 50% for the last treatment. In the last treatment, it is seen that the process also produced a significant amount of elemental sulfur.

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Table 1: Sulfur Analytical Data - Biotreated Coals
Samples from J. J. Kilbane (I.G.T.)

	III. #6 Coal Control	III. #6 Coal Biotreated	III. #6 Coal Control	III. #6 Coal Biotreated
Total S, Wt%	3.45	1.03	3.00	2.14
Organic S, Wt%	3.20	0.92	2.54	1.72
Pyritic S, Wt%	0.25	0.15	0.50	0.45

Table 2: Sulfur Forms in Gravimelt Coals from XANES Analysis

% of Total Sulfur in Different Forms

	Pittsburgh #8 2.19 wt% S	Gravimelt Pgh#8 0.43 wt% S	Gravimelt KY#9 0.70 wt% S
Pyrite	52	0	0
Elem. Sulfur	0	28	37
Org. sulfide	13	0	0
Thiophene	35	19	16
Sulfonate	0	16	14
Sulfate	0	37	33

Table 3. Weight percentages of sulfur contained in different functional forms for a number coals before and after PCE treatment, as determined from the XANES spectra. Precision estimated as ±0.2 wt.%

Sample	Pyrite	Elemental S	Sulfide	Thiophene	Sulfone	Sulfate
IBC-104 fresh	2.22*	0.0	0.72	1.18	0.0	0.11
IBC-104 2wk ox before	2.17*	0.0	0.61	1.07	0.0	0.12
IBC-104 2wk ox after	2.18*	0.0	0.61	1.12	0.0	0.07
IBC-104 5yr ox before	1.40*	0.17	0.53	0.86	0.13	1.01
IBC-104 5yr ox after	1.40*	0.0	0.56	0.88	0.07	0.41
Ohio #5/#6 before	0.79*	0.26	0.50	1.00	0.14	0.82
Ohio #5/#6 after	0.87*	0.0	0.54	1.04	0.04	0.29
Freeport, before	1.8⁺	0.65	0.25	0.85	0.0	0.2
Freeport, after	1.9⁺	0.0	0.25	0.7	0.0	0.25
Freeport, before	0.95*	0.87	0.05	0.25	0.05	0.82
Freeport, after	0.94	0.25	0.07	0.35	0.08	1.15
Indiana #5, before	0.85⁺	0.35	0.4	0.4	0.05	0.45
Indiana #5, 30 min PCE treatment	0.85⁺	0.2	0.3	0.4	0.05	0.45
Indiana #5, after	0.85⁺	0.0	0.25	0.4	0.05	0.35

⁺Pyritic sulfur values from Mössbauer spectroscopy.
*ASTM chemical analysis value

Table 4. Percentages of total sulfur contained in different functional forms (±5-10%).

| Sample	Inorganic Sulfide	Elemental Sulfur	Organic Sulfide	Thiophenic Sulfur	Sulfoxide	Sulfone	Sulfate
Illinois No. 6 raw coal	48 - pyrite	0	18	26	0	0	9
Lithium aluminum hydride (LAH) treated coal	0	0	25	66	4	3	2
SET-treated coal	15 - unk.	0	25	36	5	15	4
BASE-treated coal	18 - unk.	0	13	49	7	8	5
SET, then BASE	21 - unk.	0	24	21	11	13	10
BASE, then SET	0	9	26	36	7	9	13
Pyrite free coal + nickelocene + LAH in THF (24 hr, 67°C)	6 - unk.	0	24	47	13	9	1
Pyrite-free coal + K + napthalene + BASE in heptane (24 h, 98°C), protonated	0	23	21	32	5	10	10
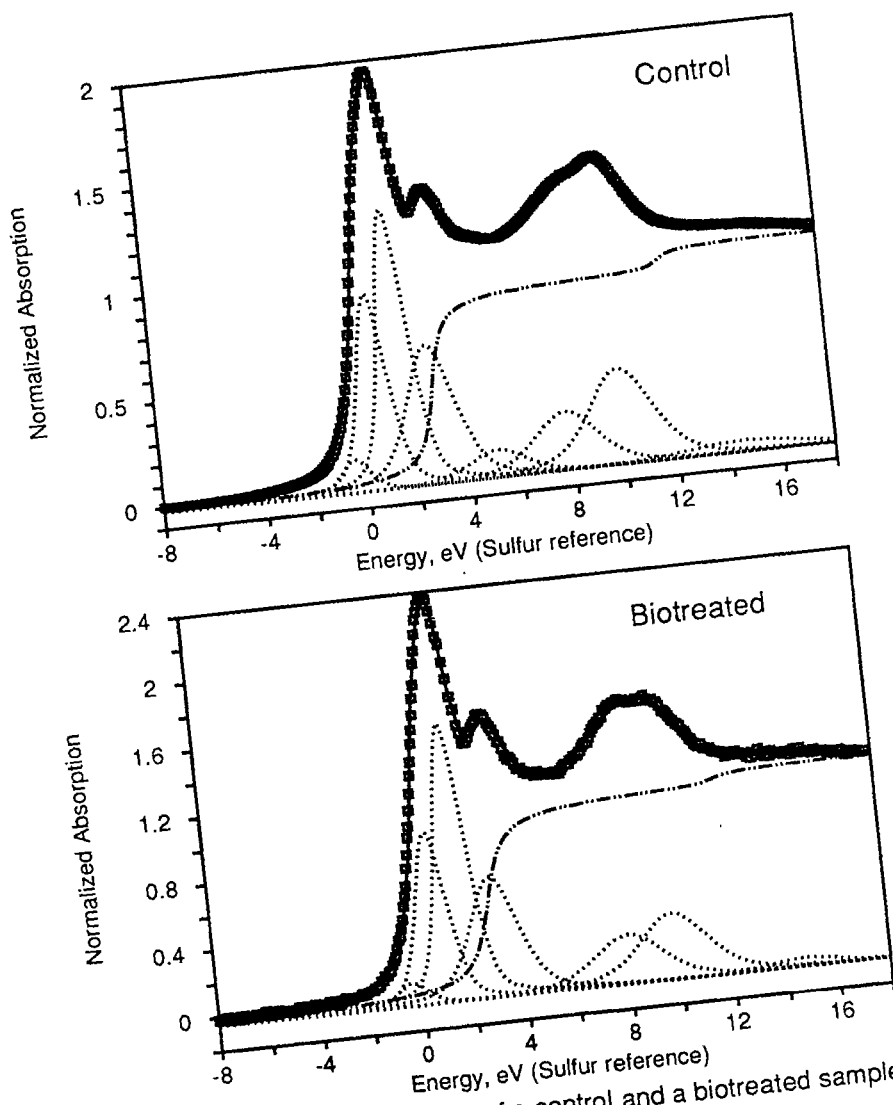
Fig 1: S K-edge XANES spectra of a control and a biotreated sample of Illinois #6 coal.
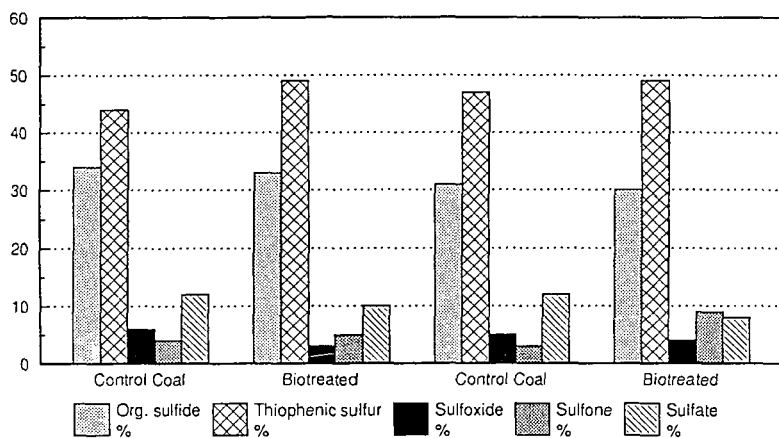
Fig. 2: Percentages of organic functional forms of sulfur in control and biotreated Illinois #6 samples as determined from the S K-edge XANES analyses.
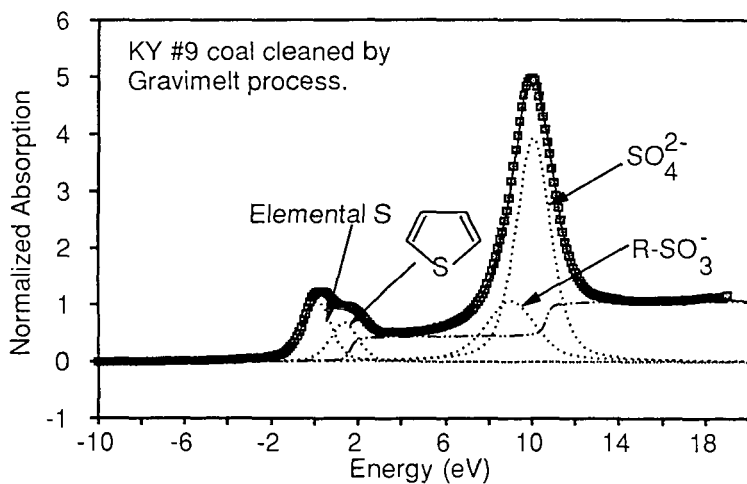

Fig. 3: Sulfur XANES spectrum of coal cleaned by molten caustic leaching.